

# (12) UK Patent Application (19) GB (11) 2 147 896 A

(43) Application published 22 May 1985

<p>(21) Application No 8425228</p> <p>(22) Date of filing 5 Oct 1984</p> <p>(30) Priority data</p> <p>(31) 58/185871 (32) 6 Oct 1983 (33) JP</p>	<p>(51) INT CL<sup>4</sup> C07C 85/06 87/20</p> <p>(52) Domestic classification C2C 20Y 287 30Y 321 322 32Y 410 413 414 416 418 41Y 456 45Y 606 640 DM NW</p>
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## (54) Process for producing diethylenetriamine

(57) Diethylenetriamine is produced by reacting monoethanolamine with ammonia in the presence of a phosphorus-containing substance and ethylenediamine at a molar ratio of ammonia and monoethanolamine of at least 11:1, preferably in the liquid phase at a temperature of 200 – 400°C and pressure of at least 200 kg/cm<sup>2</sup>G. Excellent selectivity in the production of diethylenetriamine is attained and without substantially consuming the added ethylenediamine. The product diethylenetriamine can be returned to the reaction if polyamines higher than diethylenetriamine should be desired.

## SPECIFICATION

## Process for producing diethylenetriamine

5 The present invention relates to a process for producing diethylenetriamine, in particular by ammonolysis of monoethanolamine. 5

Industrially, diethylene triamine is produced only as a by-product in the processes for producing ethylenediamine by reacting 1,2-dichloroethane with ammonia or by reacting monoethanolamine with ammonia. In the former process, a great deal of sodium chloride, up to twice the molar amount of ethylenediamine, is formed as a by-product and vinyl-chloride also is another by-product. This process becomes costly in terms of treating waste materials and has the drawback of severe apparatus corrosion by chlorine ions. Further, in both processes the production of diethylenetriamine tends to be subject to the market demand for ethylenediamine. 10

For producing diethylenetriamine, there have also been disclosed a process in which monoethanolamine is reacted with ethylenediamine using a phosphorus-containing compound such as phosphoric acid as a catalyst (Japanese Patent Publication No. 6982/1981). In another known process, monoethanolamine is reacted with ethylenediamine in the liquid phase using an inorganic compound containing alumina or silica as the main component as a catalyst (Japanese Patent Laid-open No. 38329/1980). 15

However, these processes have not yet reached a desirable level of selectivity and productivity, because, in addition to ethylenediamine being comparatively expensive, the conversion of ethylenediamine and the selectivity of diethylenetriamine are both low. 20

The process described in Japanese Patent Laid-open No. 52322/1983 improves the process described above in Japanese Patent Publication No. 6982/1981 and produces non-cyclic amines with good yields while at the same time controlling the production of cyclic amines. Ammonia at 0.5 to 10 times the molar amount of monoethanolamine used in the reaction of monoethanolamine with ethylenediamine is added in this improved process, which uses a phosphorus-containing compound such as phosphoric acid as a catalyst. In this process, however, the selectivity of diethylenetriamine is not sufficient and the consumption of monoethanolamine, ethylenediamine and ammonia in producing diethylenetriamine has the drawback of cost as expensive ethylenediamine is used as one of the raw materials. 25

The inventors have investigated various reactions of ammonia and monoethanolamine and have discovered that diethylenetriamine could be produced with remarkably high selectivity by reacting ammonia and monoethanolamine in the presence of a phosphorus-containing substance and ethylenediamine under limited reaction conditions. 30

The process of the present invention lies in producing diethylenetriamine by reacting ammonia with monoethanolamine in the presence of a phosphorus-containing substance and ethylenediamine at a molar ratio of ammonia to monoethanolamine of at least 11 to 1. 35

The present invention will now be explained in more detail in the following description, which is given by way of example only.

Phosphorus-containing substances employable in the process of the present invention include various salts of phosphoric acid, pyrophosphates, compounds of phosphoric acid or anhydrides thereof, phosphorous acid or anhydrides thereof, alkyl or aryl esters of phosphoric acid or phosphorous acid, and alkyl- or aryl-substituted phosphoric or phosphorous acid. One of these substances or a mixture thereof can be used. 40

Among the various salts of phosphoric acid, dihydrogenphosphates or compositions corresponding thereto, or pyrophosphates obtained from dehydration thereof are preferred. Among dihydrogenphosphates and their corresponding compositions, the following are exemplified: ammonium dihydrogenphosphate, lithium dihydrogenphosphate, sodium dihydrogenphosphate, potassium dihydrogenphosphate, rubidium dihydrogenphosphate, cesium dihydrogenphosphate, beryllium dihydrogenphosphate, magnesium dihydrogenphosphate, calcium dihydrogenphosphate, strontium dihydrogenphosphate, barium dihydrogenphosphate, and a reaction product of a rare earth compound with phosphoric acid, the product being a composition having an atomic ratio of 3 of phosphorus to the rare earth element. Exemplary are reaction products of phosphoric acid with a hydroxide or oxide of such elements as scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Also exemplified are manganese dihydrogenphosphate, iron dihydrogenphosphate, cobalt dihydrogenphosphate, zinc dihydrogenphosphate, cadmium dihydrogenphosphate, aluminium dihydrogenphosphate, thallium dihydrogenphosphate, tin dihydrogenphosphate, lead dihydrogenphosphate and a compound of chromium, gallium, indium, antimony or bismuth with phosphoric acid, the compound being a composition having an atomic ratio of phosphorus to the metal of 3 to 1. The compound can be a reaction product of phosphoric acid with a hydroxide or oxide of said metal. Further included are compounds of nickel or copper with phosphoric acid having an atomic ratio of phosphorus to the metal of 2 to 1, such as a reaction product of phosphoric acid with a hydroxide or oxide of said metal. 45 50 55 60

Also useful are acidic pyrophosphates obtained by dehydrating the above dihydrogenphosphates or their equivalent compositions. Further useful is a reaction product of phosphoric acid with a compound of a metal of the IVa or Va group of the periodic table of the elements, e.g. a product having an atomic ratio of P/Ti=2, 65

$P/Zr=2$ ,  $P/Hf=2$ ,  $P/V=2$ ,  $P/Nb=3$ , or  $P/Ta=3$ , such as titanyl dihydrogenphosphate or zirconyl dihydrogenphosphate.

Still further, monohydrogenphosphates may also be used. Exemplary monohydrogenphosphates include diammonium hydrogenphosphate, beryllium hydrogenphosphate, magnesium hydrogenphosphate, calcium hydrogenphosphate, strontium hydrogenphosphate, barium hydrogenphosphate, scandium hydrogenphosphate, yttrium hydrogenphosphate, lanthanum hydrogenphosphate, cerium hydrogenphosphate, praseodymium hydrogenphosphate, neodymium hydrogenphosphate, promethium hydrogenphosphate, samarium hydrogenphosphate, europium hydrogenphosphate, gadolinium hydrogenphosphate, terbium hydrogenphosphate, dysprosium hydrogenphosphate, holmium hydrogenphosphate, erbium hydrogenphosphate, thulium hydrogenphosphate, ytterbium hydrogenphosphate, lutetium hydrogenphosphate, chromium hydrogenphosphate, manganese hydrogenphosphate, iron hydrogenphosphate, cobalt hydrogenphosphate, nickel hydrogenphosphate, copper hydrogenphosphate, silver hydrogenphosphate, zinc hydrogenphosphate, cadmium hydrogenphosphate, mercury hydrogenphosphate, aluminium hydrogenphosphate, gallium hydrogenphosphate, indium hydrogenphosphate, thallium hydrogenphosphate, tin hydrogenphosphate, lead hydrogenphosphate, antimony hydrogenphosphate and bismuth hydrogenphosphate. Also usable is a reaction product of phosphoric acid with a compound of a metal of the IVa or Va group of the periodic table, e.g., a product having an atomic ratio of  $P/Ti=1$ ,  $P/Zr=1$ ,  $P/Hf=1$ ,  $P/V=1$ ,  $P/Nb=1.5$  or  $P/Ta=1.5$ .

In addition, normal salts of phosphoric acid can be used, as for example, boron phosphate, scandium phosphate, yttrium phosphate, lanthanum phosphate, cerium phosphate, praseodymium phosphate, neodymium phosphate, promethium phosphate, samarium phosphate, europium phosphate, gadolinium phosphate, terbium phosphate, dysprosium phosphate, holmium phosphate, erbium phosphate, thulium phosphate, ytterbium phosphate, lutetium phosphate, chromium phosphate, iron phosphate, aluminium phosphate and bismuth phosphate.

As compounds of phosphoric acid, the following may be included: orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid and condensed phosphoric acids such as polyphosphoric acid.

As compounds of phosphorous acid, orthophosphorous acid may be included. Further, mono-, di-, tri-alkyl or aryl esters of phosphoric acid or phosphorous acid may be used as the catalyst of the present invention, the alkyl groups being preferably those having 1 to 8 carbon atoms and the aryl groups being preferably those having 6 to 20 carbon atoms, i.e., the phenyl or alkyl-substituted phenyl group. For example, triethyl phosphate, triethyl phosphite, phenyl phosphate or phenyl phosphite may be used.

As alkyl or aryl-substituted phosphorous or phosphoric acid, the preferable alkyl and aryl groups having 1 to 8 carbon atoms and 6 to 20 carbon atoms, respectively, may be exemplified phenyl phosphinic acid, ethyl phosphinic acid, phenyl phosphonic acid and naphthaphosphonic acid.

Among the above phosphorus-containing substances, especially preferred are dihydrogen phosphates, phosphates of vanadium compounds and phosphates of rare earth compounds.

The amount of the above phosphorus-containing substance used as a catalyst may be about 0.01 to 1 mol based on phosphorus content to 1 mol of monoethanolamine as the raw material. An amount of less than 0.01 mol does not show sufficient activity while more than 1 mol may be unnecessary.

In practising the present invention, ethylenediamine is usually added in an amount of 0.1 to 5 mol to 1 mol of monoethanolamine.

If less than 0.1 mol of ethylenediamine is added the selectivity of diethylenetriamine worsens because of the production of ethylenediamine, aminoethylethanolamine, piperazine or aminoethylpiperazine as by-products. On the other hand, if more than 5 mol of ethylenediamine is added, the rate of increase of the selectivity of diethylenetriamine is not significant while the volume efficiency of the reactor worsens.

Therefore, 1 to 2 mol of ethylenediamine is preferably added.

In the process of the present invention, ammonia and monoethanolamine are caused to react with each other in a molar ratio of at least 11 of ammonia to monoethanolamine. If they react in a ratio of less than 11 to 1, ethylenediamine is consumed in large amounts, which makes the process unsuccessful. The molar ratio is preferably 11 to 30. The higher the molar ratio, the better the selectivity of diethylenetriamine but the worse the volume efficiency of the reactor. The reaction temperature is usually set at 200 to 400°C. At a temperature lower than 200°C the reaction rate is reduced, while at a temperature higher than 400°C the thermal decomposition of diethylenetriamine increases. The preferable temperature is 250 to 300°C. Although the reaction time depends on the amount of the catalyst used and the reaction temperature, about 30 minutes to 55 8 hours are usually sufficient.

The reaction may be carried out either in liquid phase or gaseous phase, but preferably in a liquid phase where the pressure is usually kept at at least 200 kg/cm<sup>2</sup>G. Since cyclic substances such as piperazine and aminopiperazine are produced in large amounts in the gaseous phase, the reaction in a liquid phase is preferred.

In carrying out the present process, both the batch system and the stream system perform acceptably, but the stream system having a fixed-bed is preferable in view of the separation of catalyst used. In this case, the space velocity of the reactants is used at about 0.1 to about 10 g total reactants/ml catalyst volume/hr, preferably about 0.2 to 2.

The above catalyst may be supported on a carrier such as diatomaceous earth, silica or alumina. Diethylenetriamine produced can be easily separated from the reaction mixture, for example, by distillation.

Since the process of the present invention has made it possible to produce diethylenetriamine from ammonia and monoethanolamine without substantially consuming expensive ethylenediamine that is added but not used as a raw material in this invention, the process has great industrial value.

The present invention is illustrated in further detail by the following examples:

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5

#### Example 1

Monoethanolamine 18.3 g (0.3 mol), ethylenediamine 18.0 g (0.3 mol) and aluminum dihydrogen phosphate 3.18 g (0.03 mol as P) were fed into an autoclave having a capacity of 300 ml with a magnetic stirrer. After the air in the autoclave was replaced by nitrogen, liquid ammonia 56.2 g (3.3 mol) was fed in and the mixture was heated to 270°C and then kept for 3 hours at that temperature, the pressure being 280 kg/cm<sup>2</sup>.G. The reaction solution was then cooled to room temperature, the pressure being reduced, and the solution was withdrawn and analyzed by gas chromatography.

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Conversion of monoethanolamine	81%
Selectivity of diethylenetriamine	70%

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Under the above conditions (NH<sub>3</sub>/monoethanolamine molar ratio of 11) ethylenediamine remained in the reaction solution in the same amount, 18.0 g, as fed in. This means that diethylenetriamine was synthesized by the reaction of only monoethanolamine and ammonia as raw materials.

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#### Example 2

The procedure described in Example 1 was repeated except that the amount of liquid ammonia was 66.4 g (3.9 mol).

Conversion of monoethanolamine	76%
Selectivity of diethylenetriamine	74%
Selectivity of ethylenediamine	2%

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Under the above conditions (NH<sub>3</sub>/monoethanolamine molar ratio of 13) the amount of ethylenediamine increased compared with before the reaction. The increased amount of ethylenediamine was 2.0% based on the converted monoethanolamine.

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#### Example 3

The procedure described in Example 1 was repeated except that the amount of liquid ammonia was 76.6 g (4.5 mol).

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Conversion of monoethanolamine	72%
Selectivity of diethylenetriamine	77%
Selectivity of ethylenediamine	4%

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#### Control 1

The procedure described in Example 1 was repeated except that the amount of liquid ammonia was 46.0 g (2.7 mol).

Conversion of monoethanolamine	86%
Selectivity of diethylenetriamine	64%

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Under the above conditions (NH<sub>3</sub>/monoethanolamine molar ratio of 9), the amount of ethylenediamine decreased compared with before the reaction. The consumed amount of ethylenediamine was 2% based on the converted monoethanolamine.

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#### Examples 4 to 24

The procedure described in Example 1 was repeated except that various catalysts used were changed, the amounts thereof being 0.03 mol as P. The results are shown in Table 1.

Example No.	Catalyst	Monoethanol-amine conversion %	Diethylene-triamine selectivity %	Ethylene-diamine selectivity %	Triethylene-tetramine selectivity %
4	$3\text{H}_3\text{PO}_4\text{-La}(\text{OH})_3$	87	66	0	17
5	$3\text{H}_3\text{PO}_4\text{-Y}(\text{OH})_3$	92	58	1	13
6	$\text{ZrO}(\text{H}_2\text{PO}_4)_2$	21	66	1	6
7	$\text{TiO}(\text{H}_2\text{PO}_4)_2$	33	77	2	7
8	$\text{VO}(\text{H}_2\text{PO}_4)_2$	78	78	4	8
9	$6\text{H}_3\text{PO}_4\text{-Nb}_2\text{O}_5$	98	60	1	9
10	$6\text{H}_3\text{PO}_4\text{-Ta}_2\text{O}_5$	93	64	1	9
11	$\text{BPO}_4$	95	70	1	11
12	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	97	55	0	12
13	$\text{LiH}_2\text{PO}_4$	87	70	0	15
14	$\text{Fe}(\text{H}_2\text{PO}_4)_3$	83	71	1	10
15	$3\text{H}_3\text{PO}_4\text{-Cr}(\text{OH})_3$	85	74	0	13
16	$\text{Ba}(\text{H}_2\text{PO}_4)_2$	68	62	0	14
17	$\text{Mn}(\text{H}_2\text{PO}_4)_2$	83	65	1	11
18	$3\text{H}_3\text{PO}_4\text{-Ce}(\text{OH})_3$	91	60	0	16
19	$\text{Pb}(\text{H}_2\text{PO}_4)_2$	83	70	0	13
20	$\text{TlH}_2\text{PO}_4$	77	74	3	8
21	$\text{FeHP}_2\text{O}_7$	65	61	0	13
22	$\text{Al}(\text{PO}_3)_3$	80	60	0	20
23	$\text{H}_3\text{PO}_4\text{-silicagel}$	86	60	0	17
24	Phenylphosphonic acid	90	60	3	15

*Control 2*

Monoethanolamine 18.3 g (0.3 mol), ethylenediamine 18.0 g (0.3 mol) and lanthanum-phosphoric acid catalyst (P/La molar ratio was 3) at 0.03 mol as P were fed into an autoclave having a capacity of 300 ml with a magnetic stirrer. After the air in the autoclave was replaced by nitrogen, liquid ammonia 25.5 g (1.5 mol) was fed in and the mixture was heated to 270°C and then kept for 3 hours at that temperature. The reaction solution was then cooled to room temperature, the pressure being reduced, and the solution was withdrawn and analyzed by gas chromatography.

10	Conversion of monoethanolamine	100%	
	Selectivity of diethylenetriamine	33%	10
	Selectivity of triethylenetetramine	8%	
	Selectivity of piperazine	14%	
	Selectivity of aminoethylpiperazine	17%	

15 Under the above conditions (NH<sub>3</sub>/monoethanolamine molar ratio of 5), ethylenediamine was consumed at 22% based on the converted monoethanolamine. Further, the selectivity of diethylenetriamine was sharply reduced and large amounts of cyclic substances such as piperazine and aminoethylpiperazine were produced.

*Control 3*

The procedure described in Example 1 was repeated except that no ethylenediamine was added.

25	Conversion of monoethanolamine	65%	
	Selectivity of diethylenetriamine	32%	
	Selectivity of ethylenediamine	44%	25

In this case, the selectivity of diethylenetriamine was also low while ethylenediamine was produced in a large amount.

*Example 25**Preparation of catalyst*

112.8 g of hexa hydrated lanthanum nitrate were dissolved in 300 ml of water to which 168 g of diatomaceous earth were added. While the slurry was being stirred, 449.5 g of a 20% aqueous solution of ammonium dihydrogenphosphate were added thereto. After the solution was heated and subjected to water evaporation, it was dried at 120°C for 3 hours and then baked at 400°C for 3 hours.

*Preparation of diethylenetriamine*

The thus prepared catalyst, with 12 - 16 mesh, P/La atomic ratio of 3, and 40% of La(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub> equivalent, supported on diatomaceous earth, was filled in an amount of 150 ml in a reactor of stainless steel with an inner diameter of 15 mm and a length of 1 m. Ammonia, monoethanolamine and ethylenediamine were fed in molar ratios of 18 of NH<sub>3</sub>/monoethanolamine and of 2 of ethylenediamine/monoethanolamine and at a velocity of the mixed feed of 1 g/catalyst ml/hr. The reactor was kept at 260°C and the reaction pressure at 320 kg/cm<sup>2</sup>G.

45 The reaction solution was analyzed with the following results:

50	Conversion of monoethanolamine	65%	
	Selectivity of diethylenetriamine	91%	
	Selectivity of triethylenetetramine	6%	
	Selectivity of ethylenediamine	2%	50

A combined fixed-bed and stream system as used in this example is preferable in producing industrial diethylenetriamine by the present invention.

If higher polyamines than diethylenetriamine are desired, it is also possible to produce them with sufficient yields by recycling the diethylenetriamine thus produced to the reactor.

**CLAIMS**

1. A process for producing diethylenetriamine, wherein ammonia is reacted with monoethanolamine at a molar ratio of ammonia to monoethanolamine of at least 11 to 1 in the presence of a phosphorus-containing substance and ethylenediamine.

2. A process as claimed in claim 1, wherein the molar ratio is in the range of 11 to 30:1.

3. A process as claimed in claim 1 or claim 2, wherein the reaction is carried out in the liquid phase.

4. A process as claimed in any of claims 1 to 3, wherein the reaction is carried out in a fixed-bed.

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5. A process as claimed in any of claims 1 to 4, wherein the reaction is carried out in a flowing stream system.
6. A process as claimed in any of claims 1 to 5, wherein the phosphorus-containing substance is a dihydrogen phosphate.
- 5 7. A process as claimed in any of claims 1 to 6, wherein the phosphorus-containing substance is a phosphate compound of rare earth element. 5
8. A process as claimed in any of claims 1 to 7, wherein products of the reaction are subjected to distillation to recover diethylenetriamine therefrom.
9. A process as claimed in claim 1 and substantially as herein described.
- 10 10. A process as claimed in claim 1 and any of Examples 1 to 25. 10
11. Diethylenetriamine when produced by the process claimed in any of claims 1 to 10.
12. A process as claimed in any of claims 1 to 10, wherein diethylenetriamine produced is fed back to the reaction for the production of higher polyamines than diethylenetriamine.